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Prediction of the viscosity reduction due to dissolved CO_2 of and an elementary approach in the supercritical CO_2 assisted continuous particle production of a polyester resin

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Abstract

The dissolution of CO_2 in a polymer causes plasticization of the polymer and hence, its viscosity is reduced. A model based on the free volume theory has been used for a polyester resin, which shows a considerable reduction in the viscosity due to dissolved CO_2. Therefore, supercritical CO_2 has been used as a processing solvent in the continuous production of micron size particles of the resin. Despite the viscosity reduction caused by the dissolved CO_2, an excess quantity of CO_2 with respect to its solubility limit has been used for micronisation of the polymer due to its high viscosity. The mixing of CO_2 and the polymer has not been possible in an extruder at high gas to polymer mass ratios and consequently, a simplified Kenics type static mixer has been used for the mixing purpose. In this study, the effect of various parameters such as temperature, pressure, nozzle diameter and gas to polymer mass ratio on the particle morphology and size has been studied. The experimental results manifest the technological as well as the theoretical insight into the particles production from a high viscosity material.

Keywords: Supercritical CO_2; Viscosity; Free volume theory; Extruder; Static mixer; Nozzle

1. Introduction

Polyester resin materials in particle form are generally used in toner and paint industries. The production of small size particles (micrometer to nanometer) on a large scale with a narrow particle size distribution is a major challenge in these industries. Various traditional particle production methods, such as milling or grinding, spray atomization and crystallization are still used. Heat dissipation during grinding or milling, emission of volatile organic components (VOCs) and separation of particles from a solvent are the major problems associated with the traditional methods.

For the past few decades, supercritical fluids are being used in various polymer applications due to their unusual properties: gas-like viscosity and liquid-like density. Various new methods to produce micron size particles that use supercritical carbon dioxide (CO_2) as a solvent have been developed in the last two decades [1,2]. CO_2 is selected as a supercritical fluid due to its inert nature, low cost and easily attainable critical conditions (P_c=7.38 MPa and T_c=304 K). Moreover, the solubility of CO_2 in many polymers is high. The dissolved CO_2 causes a considerable reduction in the viscosity, which eases the handling of viscous polymer melts. Among the various methods, the PGSS (particles from gas saturated solution) method has been reported for the batch production of and has been modified for the continuous production of particles from poly(ethylene glycol) (PEG) having different molecular weights [3]. The viscosity of the PEG (a weight average molecular weight of 6000) at 373 K is 0.574 Pa-s [4]. Unlike the batch process, an amount of gas in excess to the solubility limit has been used in the continuous process. It had a positive influence in terms of the reduction in the particle size [3].

The reduction in the viscosity of polymer due to dissolved CO_2 is one of the important parameters in the particle production and considerable attention has been given to experimental as well as to theoretical rheological studies. Various research groups have shown that the viscosity reduction of polymer melts in the presence of dissolved CO_2 could be

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understood in terms of the classical viscosity scaling theory. Gerhardt et al. [5] modified the expression developed by Kelly and Bueche [6] based on Doolittle's [7,8] free volume theory to calculate scaling factors for different CO_2 concentrations in poly(dimethyl siloxane) (PDMS). Kwag et al. [9] used the free volume theory of Gerhardt et al. [5] to obtain a master curve that relates the shear viscosity to the shear rate (η–γ) for polystyrene (PS)–CO_2 system. The predicted scaling factors using the modified free volume theory are in good agreement with experimental scaling factors for both PDMS–CO_2 and PS–CO_2 systems. Lee et al. [10] also proposed a model using the well known generalized Cross-Carreau equation [11] and Doolittle's free volume theory to describe the viscosity of PS–CO_2 system theoretically. Later, Royer et al. [12,13] developed a free volume model using the Williams–Landel–Ferry (WLF) equation [14] directly obtained from Doolittle's free volume theory and Chow's [15] model. The theoretical studies suggest that the free volume mechanism plays an important role in the reduction of polymer melt viscosity by dissolved gas. In this work, we have also used the free volume theory for predicting the viscosity reduction of a polyester resin as a function of temperature, pressure and weight fraction of the dissolved CO_2.

The other objective of this study is the particle production from a high viscous propoxylated polyester resin in a continuous manner using supercritical CO_2 as a processing solvent. The polyester resin in powder form is known for its application in toner industries. A continuous set up has been designed and constructed for the particle production using a new method. The method applied is a modification of PGSS as CO_2 in excess to its solubility limit is used. A few exploratory experiments have been performed in order to test the method and to have qualitative information over the effect of various processing parameters on the product quality.

2. Viscosity reduction theory

Scaling of isothermal shear viscosity data as a function of shear rate to a reference temperature is a general practice in polymer rheology. The curve resulting from such scaling is termed as a master curve. A similar concept has successfully been used in combination with a depression in glass transition temperature (T_g) or melting point (T_m) and free volume theory to generate a master curve using pressure and CO_2 weight fraction [9,12,13]. The master curve allows rescaling of viscosity data from a reference situation to different processing conditions.

The fact that the viscosity of polymer is a function of free volume has first been suggested by Doolittle [7,8]. The widely used William, Landel and Ferry (WLF) equation [14] can be obtained from the Doolittle theory.

$$\log a_T = \log\left(\frac{\eta_T}{\eta_{Tr}}\right) = \frac{-C_1(T-T_r)}{C_2 + T - T_r} \tag{1}$$

Where a_T and η_T are the shift factor and shear viscosity at temperature T. In case of a reference temperature (T_r) different from the T_g, the WLF parameters, C_1 and C_2, can be reduced to C_{1g} and C_{2g} using the following equations.

$$C_{1g} = \frac{C_1 C_2}{C_2 - T_r + T_g} \tag{2}$$

$$C_{2g} = C_2 - T_r + T_g \tag{3}$$

The WLF equation is generally applicable to amorphous thermoplastic polymers from its T_g up to T_g+373 K. In order to predict the viscosity reduction due to dissolved CO_2, a set of shift factor equations analogous to the WLF equation must be derived to account for the pressure effect and the T_g depression. These can be derived based on the assumption that the fractional free volume at T_g is a material constant independent of CO_2 concentration and pressure [13].

The Chow model predicts the depression in the T_g of a polymer upon the dissolution of a solvent (plasticizer). The Chow model is based on classical as well as statistical thermodynamics and has been found to be in good agreement with the reported experimental data [15–17].

$$\ln\left[\frac{T_{gmix}}{T_g}\right] = \Psi[(1-\theta)\ln(1-\theta) + \theta\ln\theta] \tag{4}$$

$$\theta = \frac{M_{pol}}{zM_{dil}}\frac{\omega_{CO2}}{1-\omega_{CO2}} \tag{5}$$

$$\Psi = \frac{zR}{M_{pol}\Delta C_{p,Tg}} \tag{6}$$

In this equation T_{gmix} is the glass transition temperature of the polymer-diluent mixture, ω_{CO2} is the weight fraction of the diluent (in this case CO_2), z is the lattice coordination parameter for the polymer repeat unit, $\Delta C_{p,Tg}$ is the change in heat capacity associated with the T_g and M_{pol} and M_{dil} are the molecular monomeric masses of the polymer and the diluent, respectively. To estimate the value for M_{pol}, the monomeric unit masses (M) and their molar fractions (x) are used.

$$M_{pol} = \sum_i x_i M_i \tag{7}$$

In the equation above the i is the number of different monomers. Using Eqs. (4)–(7), the depression in the T_g can be computed and in turn the concentration shift factor, a_C, can be calculated using the following equation in which the subscript "*co*" refers to the zero concentration of CO_2.

$$\log(a_C) = \log\left(\frac{\eta_{T,c}}{\eta_{T,co}}\right) = \frac{C_{1g}(T-T_g)}{C_{2g} + T - T_g} - \frac{C_{1g(T-T_{gmix})}}{C_{2g} + T - T_{gmix}} \tag{8}$$

The effect of pressure on the viscosity of polymer is opposite to the effect of the concentration of CO_2 and temperature. An increase in pressure decreases the free volume of the polymer

Table 1
Zero shear viscosities of PPB determined from the viscosity data obtained using a cone and plate rheometer

T (K)	η_0 (Pa-s)
363	2642.8
383	216.21
403	23.961

and increases its T_g. The effect of pressure can be incorporated in to the WLF equation by a shift in the free volume based upon a change in T_g. The T_g at different pressures can be been determined from the pressure–volume–temperature (PVT) data of the polymer. Analogy similar to the temperature effect can be used to calculate the pressure effect on the viscosity in terms of pressure shift factor, a_P.

$$\log(a_P) = \log\left(\frac{\eta_{T,P}}{\eta_{T,P0}}\right) = \frac{C_{1g}(T-T_{gmix,P0})}{C_{2g}+T-T_{gmix,P0}} - \frac{C_{1g}(T-T_{gmix,P})}{C_{2g}+T-T_{gmix,P}} \quad (9)$$

Finally, the product of the shift factors is used to generate a master curve by multiplying it with shear rates and dividing it with the viscosities obtained at the corresponding shear rates.

3. Experimental

3.1. Materials

Propoxylated polyester resin based on bisphenol (PPB, CAS: 170834-94-5) having molecular weight around 7000 (Mw–weight average) was supplied by Akzo Nobel, The Netherlands. The glass transition temperature (T_g) of the polymer is around 327 K. The zero shear viscosities of the polymer at different temperatures are provided in Table 1. High purity CO_2, 99.99%, used in the experiments was supplied by Hoekloos, The Netherlands. The materials were used without any further purification treatment.

3.2. Apparatus

In an absence of a static mixer, CO_2 is added inside an extruder. In order to inject CO_2 at an elevated pressure, the knowledge of a pressure profile and different zones in the extruder is essential. Fig. 1 shows the different zones and a typical pressure profile applicable to the addition of CO_2. The type of extruder used is twin screw counter-rotating (Rollepaal, The Netherlands). The length to diameter ratio (Le/De) of the extruder is 12. The total extruder is divided into five sections including the feed. Each section consists of a barrel surrounding the screws with a heating arrangement. The screws are fully intermeshing i.e. the gap between the core of one screw and a flight of the other screw is very small. A nozzle is attached directly at the end of the extruder.

Dividing an extruder in different zones is a normal practice in extrusion. In the low pressure (injection) zone, screw elements having a high pitch value are used. To prevent backflow of CO_2 and a polymer a high pressure build up before the injection zone is required, which can be created by a dynamic polymer melt seal (melt plug). There are various ways to create a melt plug using reverse screw elements, low pitch screw elements or a disc with circular slots.

In this study, a disc with circular slots has been used to create a melt plug before the CO_2 injection. The disc is fitted between two barrels in such a way that very small gaps are present between the circular slots made in the disc and the core of the screws. The disc is located between the two barrels distance from the feed zone. The first three barrel sections (out of five) are used to feed, transport, melt and create the melt plug. The fourth and fifth sections are used for the CO_2 injection and the mixing, respectively. After the injection zone, a pressure build up is required in order to dissolve the desired amount of CO_2 in a polymer. The diameter of the nozzle determines the pressure build up in the last section.

In the presence of a static mixer, CO_2 is added before the static mixer as shown in Fig. 2. A filter and one-way valve are connected before the injection of CO_2. The filter (pore size of 230 μm) is used to prevent choking of the nozzle caused by fine dirt, if any, present in the polymer. The one-way valve prevents

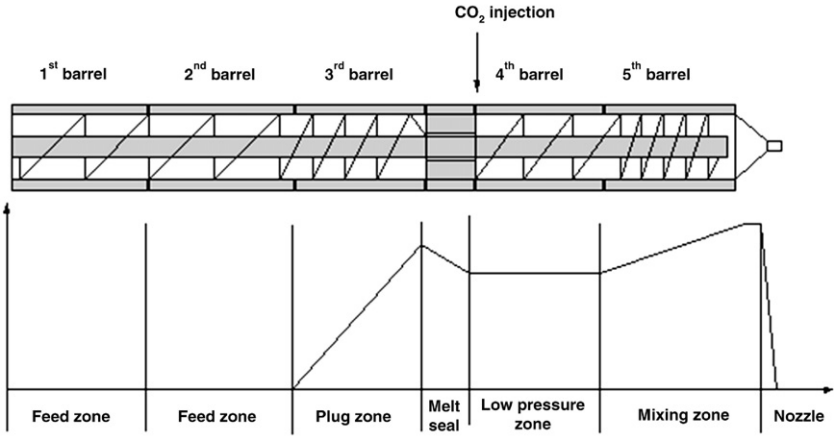

Fig. 1. A schematic drawing of the extruder divided into several sections with a pressure profile.

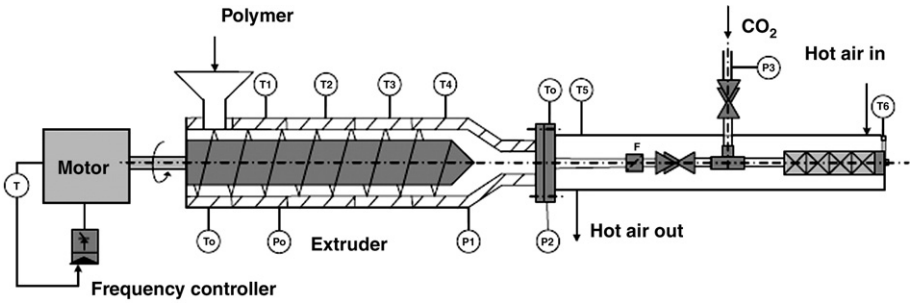

Fig. 2. A schematic drawing of the continuous particle production set up.

a backflow of the polymer towards the extruder after addition of CO_2.

Fig. 3 shows a schematic drawing of the CO_2 set up used in the continuous production of particles. In the set up, CO_2 is supplied from a bottle at 6 MPa. To prevent a cavitation problem inside a CO_2 pump (Lewa, USA), CO_2 is first cooled down to 273 K in a heat exchanger (a cooler) (Huber, The Netherlands). The mass flow capacity of the pump, membrane type, is 60 kg/h at 35 MPa. To prevent instabilities in the flow, a buffer cylinder is provided after the pump. After the buffer cylinder, a mass flow meter is installed (Danfoss: Type mass 2100, USA). The desired flow rate is controlled by using a frequency converter connected to the mass flow meter as well as to the pump. A safety relief valve is set at 34 MPa at the exit of the pump. Before CO_2 enters into the static mixer, it is heated to a desired temperature using two heat exchangers located after the pump. The temperature can be adjusted from 303 to 473 K. A pressure transducer (Dynisco, USA) is located in a CO_2-line after the third heat exchanger. The CO_2-line from the heat exchanger to the continuous particle production setup is heated using a heating element (T_{max}=473 K).

A simplified Kenics type static mixer is constructed by twisting a RVS-blade of 0.9 mm thickness in our laboratory. The constructed one and an actual Kenics static mixer are shown Fig. 4. The model mixer consists of thirteen elements perpendicular to each other with a total length of 270 mm. The diameter of the mixer is 9.0 mm and a tube around the mixer has a diameter of 9.1 mm. The main difference between the actual Kenics static mixer and the simplified one is that the elements are not alternatively turned left and right in case of the simplified one. Moreover, the length of the mixer is short. Of course, this may affect the mixing efficiency depending on the viscosity of the material.

A complete-nozzle body (Spraying systems, USA) is connected using a male–female coupling at the end of the tube surrounding the mixer. The complete-nozzle body consists of a cap, a nozzle, a core, a ring and a body as shown in Fig. 5. A nozzle has a micron size capillary hole of a very short length. An enlarged view of a core (a slot can be seen at the front side of the core) is also shown separately in Fig. 5. A core provides the extra mixing before the nozzle entrance. The width of the slots in different cores are provided in Table 2. The cores will be referred here with their names rather than with the dimensions.

3.3. Experimental method

Initially experiments were carried out in the absence of static mixer using the set up shown in Fig. 1, where a nozzle was attached to a die connected to the exit of an extruder. An experimental procedure for a continuous operation was very simple. First, a polymer was fed by a hopper (K-Tron Feeder,

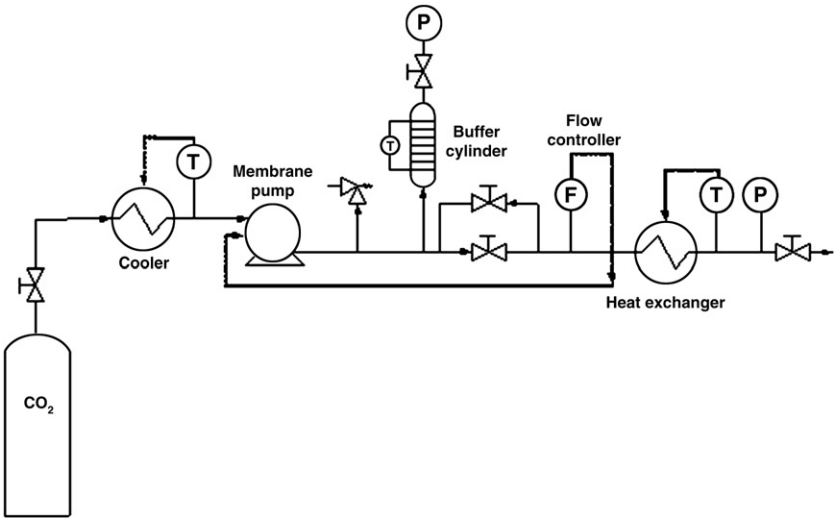

Fig. 3. A schematic drawing of the CO_2 set up used in the particle production.

The Netherlands) that was calibrated for the mass flow of 1–10 kg/h. The revolution velocity of the extruder was varied between 15 and 50 rpm. The four sections and the die at the end of the extruder were kept at 363, 368, 373, 378 and 378 K, respectively. This is the minimum temperature profile possible with the present extruder without cooling. It was observed that the selected temperature profile could provide a minimal backflow in the extruder due to high viscosity of the polymer. In the experiments, the temperature of the mixture was varied between 363 and 423 K. A pressure build up in the set up was mainly decided by the nozzle resistance and the viscosity of the polymer. The constant pressure at the last section of the extruder indicated a stable flow rate. Subsequently, CO_2 was injected initially at a gas to polymer mass ratio smaller than unity using the membrane pump and the mass controller. In the absence of and presence of the static mixer CO_2 was added inside the extruder and after the extruder, respectively. The mass ratio was increased to higher values until small fibers or particles were produced. The production of the fibers or particles was possible at and above the mass ratio of 3. Pressure and CO_2 flow rate stabilities in the CO_2-line were an indication of a steady condition. The CO_2-polymer mixture was continuously expanded into a Perspex drum, where the particles were collected.

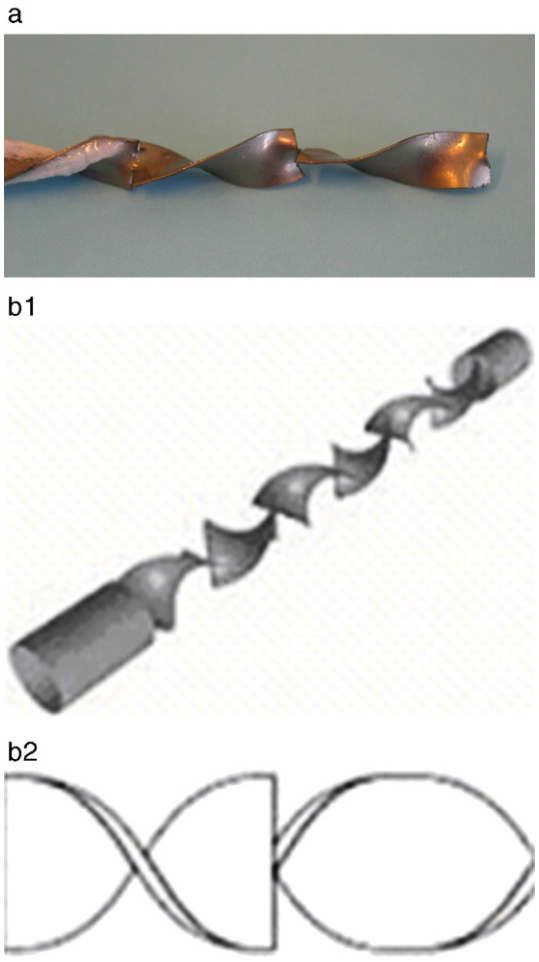

Fig. 4. (a) A constructed static mixer (b) the Kenics static mixer with an enlarged view of right and left element arrangement.

Fig. 5. (a) A complete nozzle body (b) an enlarged view of a core.

3.4. Particle analysis

A wet laser diffraction (WLD) apparatus, Malvern Mastersizer®, was used for the particle size measurement. During the measurements, a continuous recirculation of a liquid containing a suspension of particles was provided in order to scan the particles for a large number of times. A few drops of a surfactant were added to demi-water (solvent) to prevent agglomeration of particles during the measurements. However, the possibility of agglomeration cannot be avoided due to a hydrophobic nature of the polymer. The average diameter of the particles ($d_{p,0.5}$) was determined from the cumulative volume fraction. A scanning electron microscope (SEM) was specifically used to observe the morphology of the particles.

4. Results and discussions

The model based on the free volume theory has been used to calculate the reduction in the shear viscosity of PPB as a function of the weight fraction of the dissolved CO_2. Since the residence times of CO_2 and polymer are generally very short in a continuous operation, the degree of mixing achieved during the process is very important. There have been two possibilities available for the mixing. The first is to mix inside an extruder in the absence of a static mixer. High shear generated in the extruder is used to break up the dispersed (gas) phase. A further break up of these gas bubbles results into enhanced mass transfer of gas into polymer. The second possibility is using a static mixer that is also widely used for mixing materials having different viscosities.

4.1. Viscosity prediction results

Recently, it has been reported by several research groups that a master curve also exists for the experimental rheological data of a

Table 2
The width of the slots in different cores used in the particle production

Core	Slot width (mm)
A	0.41
B	0.51
C	0.64

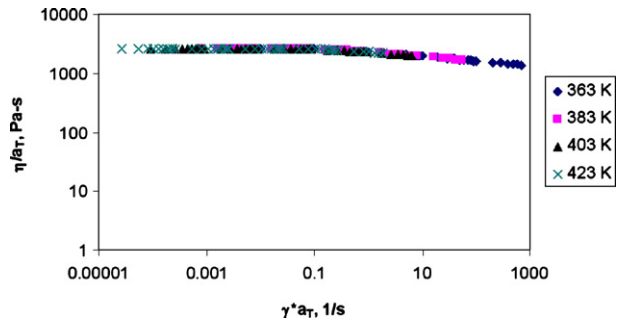

Fig. 6. A master curve generated using the experimental viscosity data measured in absence of CO_2 for PPB.

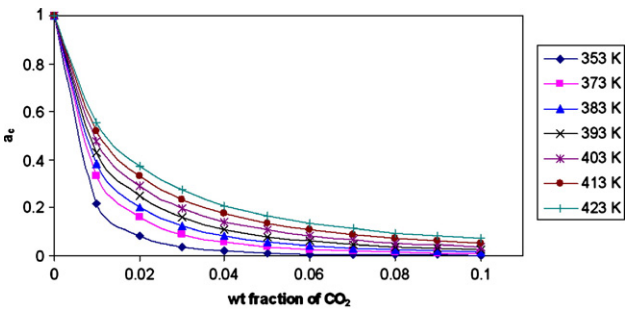

Fig. 7. Predicted a_c shift factors under different isothermal conditions for PPB.

polymer–CO_2 solution if the effect of temperature, pressure and CO_2 weight fractions are considered together [5,9,10,12,13]. The theory discussed here has been successfully applied to several polymer–CO_2 solutions in order to generate a master curve using the physical properties of the pure components. In this work, the viscosity data of the pure polymer melt have been rescaled from a reference condition to different processing conditions using the shift factors calculated from the physical properties of the pure components.

Fig. 6 clearly shows that a master curve for temperature exists for the rheological data obtained at different temperatures for pure PPB melt in the absence of CO_2. It has been used to calculate the WLF parameters. The fractions of the monomeric units in the polymer have been determined by ^{1}H NMR. The polymer repeat number, z, can be estimated as, the closest integer number, the ratio of the molecular size of the average monomeric unit relative to CO_2 [5]. The size of the monomeric units and CO_2 have been estimated with the help of a computer program (ACD/3D). Table 3 provides the estimated values of M_{pol} and Z for PPB. The a_c and a_p predicted using the model based on the WLF theory and the Chow model are shown in Figs. 7 and 8.

The predicted results suggest that the a_p increases with increasing pressure and a_c decreases with increasing CO_2 weight fraction. Thus, the theory predicts that the CO_2 dissolution decreases the glass transition temperature, while an increase in pressure increases the glass transition temperature. An increment and a reduction in free volume, due to dissolved CO_2 and pressure, respectively, are responsible for such effects. The predicted zero-shear viscosities using a_p and a_c values at different CO_2 weight fractions under isothermal conditions are shown in Fig. 9. It can be seen from the predicted viscosity curves that a considerable reduction in the zero-shear viscosity takes place with increasing CO_2 weight fraction. However, the reduction in the viscosity is smaller at higher CO_2 concentration as the pressure effect starts to dominate at higher pressures. Though the theoretical estimated data have not been tested here with experimental data, the estimates favor the possibilities of processing PPB with supercritical CO_2.

Table 3
Estimated polymer repeat unit (Z) and average monomer mass (M_{pol}) for PPB

Polymer	z (–)	M_{pol} (g/mol)
PPB	4	226.57

4.2. Twin screw extruder results

The mixing in an extruder is influenced by a number of parameters such as the number of screws, screw configuration, number of mixing elements, residence time, etc. A twin screw extruder is a suitable choice compared to a single screw extruder. In twin screw extruders the mixing efficiency is higher due to more shear regions (between barrel and screws, and between the screws). In this study, a high viscous material (polymer) has been mixed with a very low viscous fluid (CO_2) at elevated pressures.

Since the Le/De ratio of the available extruder is small, problems such as a backflow and short residence time are expected. A few experiments have been carried out to test the viability of the extruder setup. During the experiments, the amount of CO_2 added has been varied from a low to a high flow rate. It has been possible to add CO_2 only up to 1 kg/h. The added amount of CO_2 has not been sufficient to produce particles. However, micron size fibrous particles along with foam has been produced around the supercritical pressure. At higher CO_2 flow rates, a backflow of the polymer and CO_2 has been observed due to a large reduction in the viscosity of the polymer–CO_2 solution. The set up is suitable for low CO_2 flow rates, which are required in case of a microcellular foaming application [18–21]. In further experiments, CO_2 has been added after the extruder before the static mixer to increase the flow stability.

4.3. Static mixer (Kenics type) results

The experimental results obtained using different nozzle diameters in the presence of the static mixer are given in Tables 4, 5 and 6. From the Tables, it can be seen that it is not possible to produce particles for all experimental conditions. A

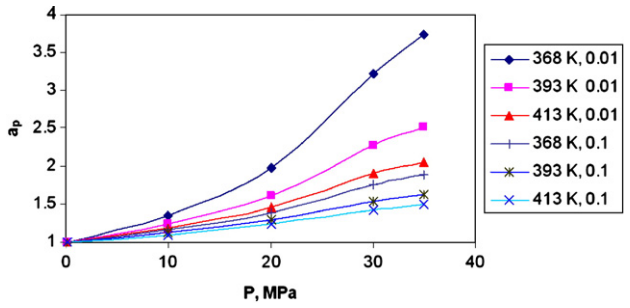

Fig. 8. Predicted a_p shift factors under different isothermal conditions and CO_2 weight fractions for PPB.

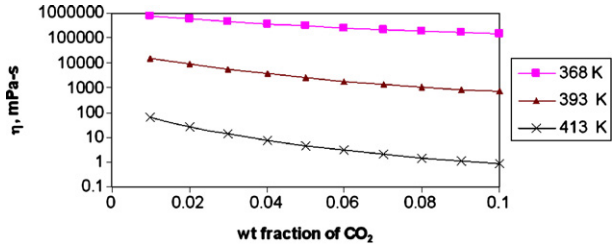

Fig. 9. Zero-shear viscosity data for PPB–CO_2 rescaled from the viscosity measured at 363 K in the absence of CO_2 using shift factors.

principal component analysis, a descriptive statistical technique, has been used to differentiate products as a function of various parameters. Also, the effect of various parameters such as nozzle diameter, core-slot width, gas to polymer mass ratio (GTP), temperature (T) and pressure (P) on the product shape and size have been discussed.

4.3.1. Principal component analysis (PCA)

In the last century, principle component analysis (PCA), one of the multivariate methods, has first been described by Pearson [22]. PCA allows clustering of the data by playing with the variables used. The analysis uses the combination of standardized dimensionless variables to produce indices that are uncorrelated. The indices are called principal components and are linear function of variables. The standardized dimensionless variables are obtained from the original data using the variables mean values and the standard deviations. The comprehensive details of PCA with different examples have been given elsewhere [23]. At the end of the analysis, two principal components with larger variances are selected to represent the dependency of an output on the variables. The important thing in this analysis is that a large number of variables are represented by two dimensionless indices, the principal components. Moreover, it uses correlativity, positive or negative, between the variables.

Table 4
Experimental results obtained with the 0.40 mm diameter nozzle

Exp.	GTP $\left(\frac{kg/hr_{CO_2}}{kg/hr_p}\right)$	Core	T (K)	P (MPa)	Product
1	3.00	C	393	18.40	Foam
2	1.00	C	404	14.55	Foam
3	3.00	C	405	17.40	Agg. fibers
4	4.00	C	404	19.20	Agg. fibers
5	0.95	C	412	13.50	Foam
6	1.40	C	413	13.60	Foam
7	2.00	C	413	14.40	Foam
8	3.00	C	413	16.50	Agg. fibers
9	0.33	C	422	12.30	Foam
10	1.00	C	421	12.80	Foam
11	1.00	C	421	12.75	Foam
12	1.50	C	424	12.95	Foam
13	1.60	C	422	14.10	Foam
14	2.00	C	423	14.75	Foam+agg. fibers
15	2.10	C	422	13.60	Foam+agg. fibers
16	3.00	C	423	17.75	Less agg. fibers
17	3.00	A	423	16.20	Less agg. fibers

Table 5
Experimental results obtained with the 0.57 mm diameter nozzle

Exp.	GTP $\left(\frac{kg/hr_{CO_2}}{kg/hr_p}\right)$	Core	T (K)	P (MPa)	Product
18	1.40	–	395	12.65	Foam
19	2.10	–	394	13.05	Foam
20	2.80	–	393	13.90	Foam with fibers
21	4.00	–	404	11.25	Less agg. fibers
22	3.00	–	406	11.95	Less agg. fibers
23	4.00	–	405	16.45	Less agg. fibers
24	3.75	–	414	14.55	Less agg. fibers
25	3.00	–	416	12.40	Less agg. fibers
26	3.00	B	397	12.50	Less agg. fibers
27	4.00	B	398	14.75	Less agg. fibers
28	3.00	B	403	12.35	Less agg. fibers
29	3.00	C	421	7.60	Less agg. fibers

In this study, the PCA has been used to describe qualitatively over the possibility of foam or fibers or particles production. Cs, Ts, GTPs, Ps and d_ns are the standardized dimensionless variables of core-slot width, temperature, gas to polymer mass ratio, pressure and nozzle diameter, respectively used in this analysis where all having a standard deviation of 1. Two principal components as a function of standardized variables are given in Eqs. (10) and (11).

$$Z1 = -0.491*\mathrm{Cs} - 0.534*\mathrm{Ts} + 0.418*\mathrm{GTPs} - 0.187*\mathrm{Ps} + 0.514*d_n s \quad (10)$$

$$Z2 = 0.084*\mathrm{Cs} + 0.041*\mathrm{Ts} + 0.0506*\mathrm{GTPs} + 0.857*\mathrm{Ps} + 0.024*d_n s \quad (11)$$

$Z1$ and $Z2$ determine the morphology of the final product. Using the $Z1$ and $Z2$, a possible grouping of different morphologies is shown in Fig. 10. It is clear from Fig. 10 that the particles are mostly produced for the positive values of $Z1$ (>2) and $Z2$ (>0) and the foam is mostly produced for the negative values of $Z1$ (<0) and the positive values $Z2$ (>0). The fibers (agglomerated fibers) are present between the foam and the particles. These results are sufficient to preliminarily choose conditions depending on the desired product.

Table 6
Experimental results obtained with the 0.81 mm diameter nozzle

Exp.	GTP $\left(\frac{kg/hr_{CO_2}}{kg/hr_p}\right)$	Core	T (K)	P (MPa)	$d_{P,05}$ (μm)	Product
30	4.21	–	373	10.7	–	Foam
31	2.00	–	392	8.35	–	Foam+particles
32	3.00	–	392	9.40	–	Foam+particles
33	3.00	B	395	9.55	137.4	Particles
34	3.00	B	399	9.30	157.9	Particles
35	3.00	B	398	11.65	133.5	Particles
36	3.00	B	404	9.20	150.9	Particles
37	3.50	B	402	11.85	128.8	Particles

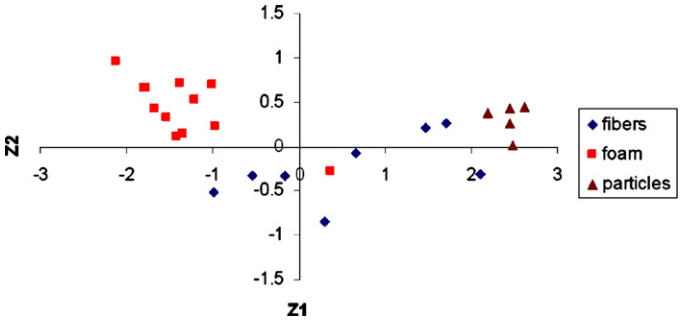

Fig. 10. Plot of the PCA results, particles, fibers and foam, for the two principal components, Z1 and Z2.

4.3.2. Elementary study of various parameters affecting the product quality

Tables 4, 5 and 6 clearly show the dependence of product quality on the core and nozzle diameter. In the presence of a core, the quantity of foam produced along with particles is reduced compared to similar conditions in the absence of a core. The slots present in the core, causes splitting of the stream before the nozzle entrance, provides an extra homogenization of excess CO_2 and a CO_2-saturated polymer solution. This results into a better expansion. However, a small amount of foam was present in the product. Therefore, the product was always screened through a 900 μm size sieve.

In PGSS, a single-phase solution of a polymer and CO_2 is expanded over a nozzle in order to produce particles. Such expansion is dependent on the shear viscosity of the polymer solution. In case of high molecular weight polymers both shear and extensional viscosity inhibit the break up of a polymer solution. Since the shear viscosity of PPB is very high, an excess of CO_2 is necessary in order to break up the polymer melt. For PPB, it is possible to have a continuous expansion at a gas to polymer mass ratio equal to or higher than 3 only. Since an excess of CO_2, unlike PGSS, is used in this method for the particle production, the method has been termed as expansion of gas-saturated solution with excess gas (EGSEG).

The effect of increasing gas to polymer mass ratio (GTP) on the flow behaviour is shown schematically in Fig. 11. Increasing the ratio, a transition from one flow regime to another takes place in the nozzle. From Tables 4, 5 and 6 it can be seen that at smaller ratios (<3) mostly foam is present while the particles are produced as the ratio is increased. At higher ratios, the expansion of excess CO_2 causes intense instabilities at the surface of the polymer melt present in the form of a thin film and hence, the break up of the polymer melt is enhanced. However, it should be noted that the foam is produced even at higher ratios if the temperature and pressure are low, for example experiments 1 and 30.

A considerable effect on the product quality is also observed in terms of the nozzle diameter. For example, the scanning electron microscope results of experiments 3, 28, 33 and 36 are shown in Fig. 12. As the nozzle diameter is increased, the product is changed from agglomerated fibers to irregular shaped particles. The results can be explained considering the extensional viscosity (viscoelasticity) of the polymer, which also plays an important role in the breakup of a polymer solution [24,25]. A schematic drawing of the elongation of polymer molecules is shown in Fig. 13. Mansour and Chigier [24] have concluded from their study that a very large stretching motion takes place before the break up in case of viscoelastic materials compared to viscoinelastic materials. Before the break up of a viscoelastic material, long threads are always formed along with droplets and thus, the breakup is inhibited. This is mainly caused by the molecular orientation under an extensional effect.

Polymer molecules, which are long chains intermingled into each other, entering a nozzle are subjected to elongation if the flow converges from a large to a small cross section. The smaller the diameter of the nozzle the higher is the extensional effect experienced by the polymer molecules. Moreover, a high shear experienced by the polymer molecules inside a small diameter nozzle keeps the molecules align. Such elongation prevents the breakup of a polymer solution into particles even at elevated pressures and hence, agglomerated fibers are formed. Not only extensional viscosity but shear viscosity also plays an important role in the particle production. The lower the shear viscosity of a polymer the easier is the break up of the polymer melt into particles. It has already been mentioned in the text that it is not possible to produce particles at low temperatures even with high gas to polymer mass ratios with a bigger diameter nozzle where the extensional effect is a less pronounced. It clearly indicates that shear viscosity must also be reduced sufficiently in order to produce particles. The viscosity model predicts a considerable reduction in the viscosity in the presence of dissolved CO_2.

The higher the temperature the lower is the shear and extensional viscosity. Thus, it is more easy to break up a polymer melt into particles at high temperatures. Less agglomerated product is obtained at a high temperature for 0.4 mm diameter nozzle as shown in Fig. 14. It is also expected that at higher temperatures the mixing efficiency increases because of a low shear viscosity, not only caused by an increase in temperature but also by the dissolved CO_2, which results into a better expansion. In case of 0.4 and 0.57 mm diameter nozzle, it is difficult to check the effect of pressure and temperature on the particle size due to an agglomerated fibrous product. The agglomerated fibers are hollow in a longitudinal direction, which also confirms the extensional effect. Due to an elongation

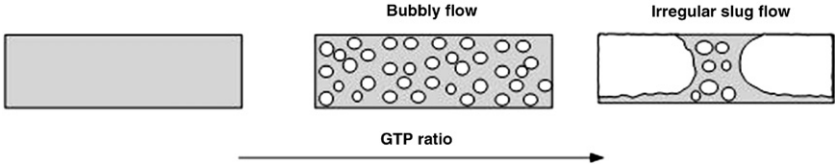

Fig. 11. Different flow regimes in a nozzle with increasing gas to polymer mass ratio.

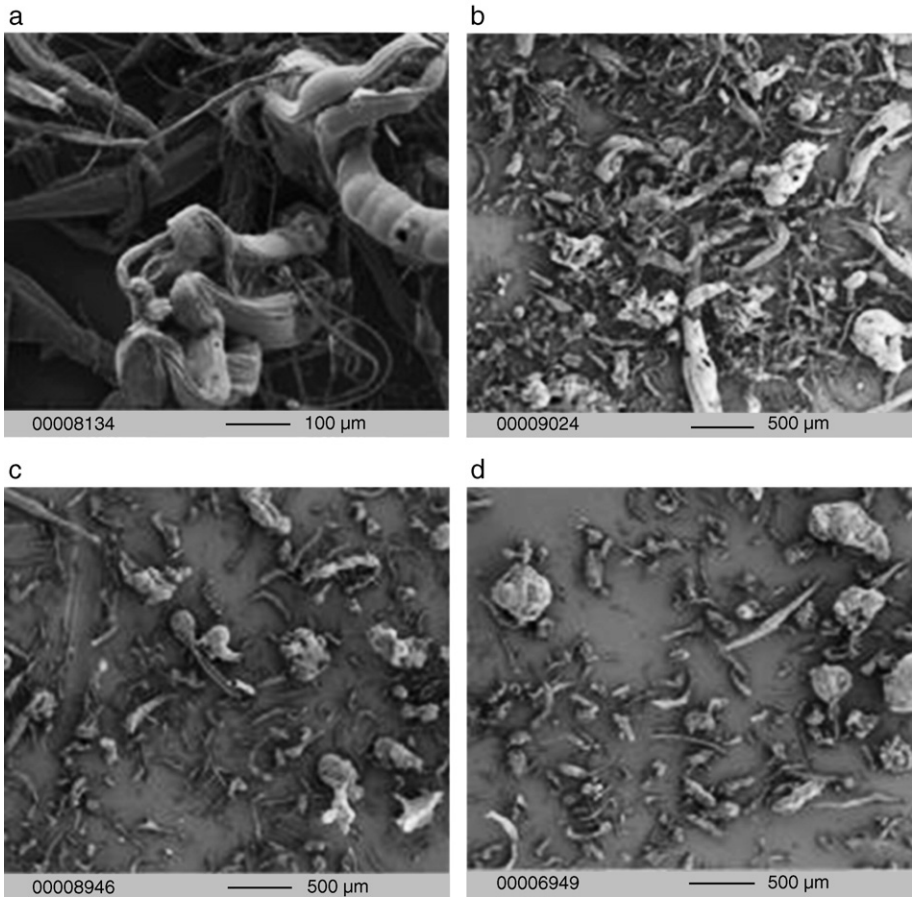

Fig. 12. Scanning electron microscope pictures of the product obtained using different diameter nozzles (a) 0.4 mm (exp. 3) (b) 0.57 mm (exp. 29) (c) 0.81 mm (exp. 37) (d) 0.81 mm (exp. 34).

of polymer molecules it is difficult for CO_2 to escape out from the surface of the melt and consequently, a longitudinal path is preferred by the CO_2 for its diffusion. The fibrous product is easily crushable to very fine powder even with a very low shear.

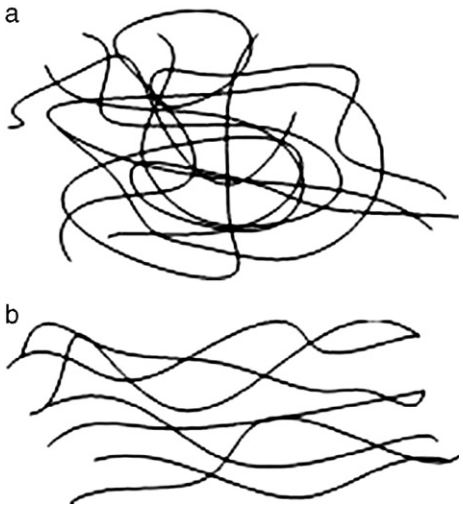

Fig. 13. A schematic drawing of the elongation of polymer molecules in a small diameter nozzle (a) before entering a nozzle (b) after entering the nozzle: extensional and shear effect.

The low-density product is mainly due to the CO_2 captured inside the fibers during solidification.

Relatively smaller differences are observed in terms of the average particle diameter ($d_{p,0.5}$) affected by temperature or pressure for a nozzle with a diameter of 0.81 mm, Table 6. The particle size distributions obtained using the traditional grinding and the EGSEG method under different conditions are shown in Fig. 15. No considerable effect of the temperature and the

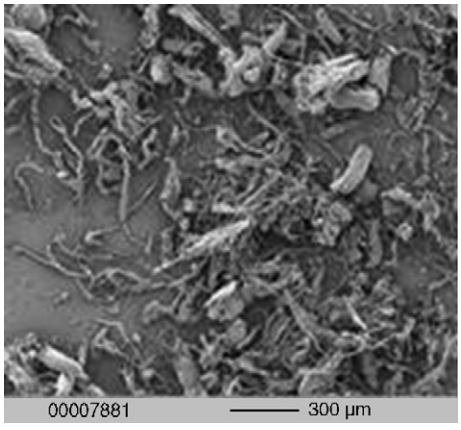

Fig. 14. Scanning electron microscope picture of the product obtained using a 0.4 mm diameter nozzle (experiment 16).

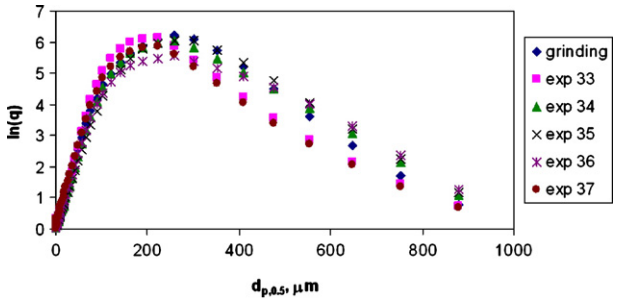

Fig. 15. Particle size distributions obtained using a 0.81 mm nozzle diameter under different processing conditions and grinding method.

pressure are present. The key advantage of the new method is the single step process, whereas the traditional method requires a large number of recycles. Moreover, the EGSEG method allows controlling the shape, size and density of the particles. The pressure and the mixing inside the static mixer are the limiting factors of the set up studied. Better results, i.e. a further reduction in the particle size and a narrower particle size distribution, are expected at higher pressures.

5. Conclusions

The model based on the free volume theory clearly indicates the plasticization of the polymer due to dissolved CO_2. The continuous micron size particle production from the high viscous polymer using CO_2 as a supercritical fluid is possible by modifying PGSS. An inert nature, a low cost and easily attainable supercritical conditions are the crucial factors responsible for the selection of CO_2. Unlike PGSS, CO_2 in excess to its solubility are essential in the break up of the high viscous polymer solution. The principle component analysis predicts different regions for formation of foam, fibers and particles. The extensional and shear viscosity, solubility, nozzle diameter, pressure and temperature play important roles in the break up of polymer solution. For the experiments studied, the effect of pressure and temperature on the particle size and particle size distribution is absent. This study provides a good insight into the particle production from a high viscous polymer melt using supercritical CO_2.

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